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(21) International Application Number: PCT/GB98/01258 (22) International Filing Date: 13 May 1998 (13.05.98) (30) Priority Data: 9709853.7 15 May 1997 (15.05.97) GB (71) Applicant (for all designated States except US): DE SAN-GOSSE UK S.A. [FR/GB]; Market Weighton, P.O. Box 135, York YO4 3YY (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): BOWEN, Ivor [GB/GB]; 23 Maes Cadwgan, Creigiau, Cardiff CF4 8TQ (GB). (74) Agent: BROWNE, Robin, Forsythe; Urquhart-Dykes & Lord, Tower House, Merriion Way, Leeds LS2 8PA (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: MOLLUSCICIDES			
(57) Abstract			
<p>A molluscicide containing a non-toxic animal repellent and metaldehyde, in which the molluscicidal efficacy of the molluscicide is greater than that of the molluscicide if it did not contain repellent. The repellent may be an anthranilate compound or d-pulegone which is present at a concentration of up to 1 %.</p>			

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Molluscicides

This invention relates to molluscicide formulations and in particular to molluscicide formulations for agricultural and horticultural purposes which act to repel non-targeted species while having an increased efficacy in killing a targeted species.

Prevention of damage to seeds and crops includes control of avian depredation and mammalian seed predators as well as consumption by mollusca. However, the ingestion of pesticides by non-targeted species can limit the use of such agricultural chemicals. To this end, a molluscicide formulation which concomitantly provides a non-toxic repellant to birds and mammals fulfils a need. Such a molluscicide formulation has advantages such as more specific targeting for a particular species, acting as a repellant to avert other species and being non-toxic to other species thereby reducing the hazard for non-targeted species.

According to a first aspect of the invention there is provided a molluscicide formulation containing a non-toxic animal repellant and metaldehyde. It has been found that combining a non-toxic animal repellant with metaldehyde in a molluscicide formulation has a synergistic effect on the efficacy of the molluscicide formulation; i.e. the molluscicide formulation kills a greater number of mollusca than if the molluscicide formulation did not contain the repellant. The animal repellant may be a bird and/or mammal repellant

Such a molluscicide formulation has a number of advantages. It is more efficient at killing a targeted pest and so reduces damage to crops and seeds. It also helps to avert avian and mammalian pests from crops and seeds and so reduces damage by the pests. Further, as the repellant is non-toxic to avian and mammalian species it does not provide a hazard to them and so

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may be employed as a pesticide in situations in which toxic repellents may not be used.

The repellent may be an anthranilate compound. Preferably the anthranilate compound is selected from methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate and dimethyl anthranilate. More preferably the repellent is methyl anthranilate or dimethyl anthranilate. Methyl anthranilate is a non-lethal bird repellent. Anthranilate derivatives are generally non-toxic. Methyl anthranilate is also biodegradable affording no detectable residues and therefore poses little environmental threat. Although methyl anthranilate is non-toxic, it has been found that at relatively low concentrations it acts synergistically with metaldehyde to improve molluscicidal efficacy as well as targeting and so may greatly enhance the environmental profile of molluscicides.

In preferred embodiments of the invention, the repellent is d-pulegone. This repellent is a potent non-toxic bird repellent and is used as a harmless mint flavouring in human foods. The compound is a non-phytotoxic terpenoid and comes from the pennyroyal plant (*Mentha pulegium*). It is used at concentrations greater than 1% in food preparations. Concentrations as low as 0.01% have been shown to repel birds significantly and the compound has also been shown to repel dogs. D-Pulegone has been found to perform at least as well as anthranilate compounds in terms of molluscicide synergy and to be better at lower concentrations. It is 10 times as efficient a bird repellent as dimethyl anthranilate and comparatively inexpensive leading to cheaper molluscicide formulations.

The repellent may be present at a concentration of not more than 1%. Preferably the repellent is present at a concentration of not more than 0.5%. Such low concentrations of repellent have been found to satisfactorily avert avian and mammalian pests and results in a cheaper molluscicide.

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Percentages and amounts used in this specification are by weight unless indicated otherwise.

The metaldehyde may be present at a concentration of not more than 6%. The metaldehyde may be present at a concentration of not more than 4%. The metaldehyde may be present at a concentration of not more than 2%.

According to a second aspect of the invention there is provided use of a molluscicide formulation consisting essentially of a non-toxic animal repellent and metaldehyde.

The animal repellent may be selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate, dimethyl anthranilate and d-pulegone.

The repellent may be present at a concentration of not more than 1%, preferably not more than 0.5%.

The metaldehyde may be present at a concentration of not more than 6%, preferably not more than 4%, or more preferably not more than 2%.

According to a third aspect of the invention there is provided a molluscicide formulation comprising 92-96.5% flour, 6-2% metaldehyde, 1-0.5% non-toxic animal repellent and 1% calcium propionate

The invention is further described by means of example, but not in any limiting sense, with reference to the accompanying drawings, of which:

Figures 1-3 show a comparison of the mortality and grain loss rate in repellent and none repellent containing molluscicide formulations; and

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Figure 4 shows a comparison of the efficacies of different amounts of metaldehyde in a repellent containing molluscicide formulation.

The synergistic advantage of combining a non-toxic bird and mammal repellent with a metaldehyde based molluscicide formulation has been demonstrated using a well established technique which simulates controlled field conditions.

Pellets were prepared by mixing Durum wheat flour with the following non-toxic repellents:

1. Methyl anthranilate (99.0% pure) BR1
2. Dimethyl anthranilate (95.0% pure) BR2
3. Methyl/Dimethyl Anthranilate (starch encapsulated at 19% w/w) BR3
4. D-Pulegone (95.0% pure) BR4

to give final concentrations of the repellents of 0.5% and 1%. Metaldehyde was added to the flour/repellent mixtures and thoroughly mixed to provide 2% and 4% metaldehyde w/w. The mixture was then compressed into small pellets having approximate dimensions of 5mm by 2mm. Similar pellets were made from metaldehyde and flour mixtures and flour only to provide control samples. The efficacy of the pellets was then tested in standardised terraria.

Test terraria in the form of trays measuring approximately 0.2m² had 100 wheat grains sown on a double thickness of filter paper as a test crop. Pellets were randomly added at the commercially recommended rate of approximately 200 g/100 m². Five pre-starved slugs within a narrow weight band were introduced per terrarium tray and two trays per category per replicate were used. This rate represents a heavy slug infestation of 400,000 per hectare in the field. A total of three replicates were undertaken at 17°C. Using this technique the molluscicidal efficacy of 0.5% and 1% concentrations of the

Table 1: Mean data of three terraria trials showing slug mortality and grain loss.

				ALL FORMULATIONS CONTAIN 4.0% Metaldehyde											
				X						X					
	DAYS	CONTROL Blank	4.0% Metaldehyde	0.5% METHYL ANTHRANILATE	1.0% METHYL ANTHRANILATE	0.5% DIMETHYL ANTHRANILATE	1.0% DIMETHYL ANTHRANILATE	0.5% METHYL/DIMETHYL ANTHRANILATE	1.0% METHYL/DIMETHYL ANTHRANILATE	0.5% D-PULEGONE	1.0% D-PULEGONE	0.025% BITREX	0.050% BITREX	0.5% CINNAMAMIDE	1.0% CINNAMAMIDE
MORTALITY %	1	-	63.3	70.0	55.0	83.3	66.7	66.7	53.3	63.3	70.0	53.3	60.0	63.2	50.0
	2	-	73.7	96.7	63.3	90.0	83.3	90.0	76.7	96.7	90.0	80.0	80.0	80.0	66.7
	3	-	86.7	100.0	80.0	90.0	90.0	90.0	86.7	100.0	93.3	90.0	83.3	86.7	80.0
	4	-	93.3	100.0	90.0	96.7	100.0	100.0	90.0	100.0	93.3	90.0	90.0	86.7	83.3
	5	-	96.7	100.0	90.0	96.7	100.0	100.0	93.3	100.0	96.7	90.0	90.0	90.0	90.0
	6	-	96.7	100.0	93.3	96.7	100.0	100.0	96.7	100.0	96.7	93.3	90.0	93.3	90.0
	7	-	100.0	100.0	93.3	100.0	100.0	100.0	96.7	100.0	96.7	93.3	90.0	93.3	93.3
GRAIN LOSS (%)	1	10.7	2.3	0.7	2.7	1.0	1.7	1.3	2.3	2.0	2.0	1.3	1.3	1.3	2.3
	2	32.3	3.7	2.0	5.0	2.3	3.3	3.3	9.7	2.3	3.3	5.0	4.3	3.7	8.0
	3	46.3	4.3	2.0	6.7	2.6	4.0	4.0	12.3	2.3	4.0	6.3	4.6	6.0	9.3
	4	55.0	5.0	2.0	8.7	3.0	4.3	4.3	16.0	2.3	4.0	7.3	4.6	6.7	9.7
	5	56.7	5.0	2.3	8.7	3.0	4.3	4.3	17.0	2.3	4.0	9.0	4.6	7.0	9.7
	6	64.0	5.0	2.3	8.7	3.3	4.3	4.3	17.0	2.3	4.3	9.0	4.6	7.0	9.7
	7	69.7	5.0	2.3	8.7	3.3	4.3	4.3	17.0	2.3	4.3	9.3	5.0	7.0	10.3
NON-VIABLE GRAINS (%)		3.0	7.6	7.0	5.3	3.3	2.7	4.3	0.7	2.7	3.0	0.3	2.3	5.7	5.7
MICROBIAL INFECTION (%)		1.0	1.0	0.3	0.7	1.3	0.7	1.0	0.7	-	0.3	0.7	-	1.0	2.0

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different repellents in a 4% metaldehyde molluscicide formulation was investigated by comparison with flour and metaldehyde pellets and flour pellets.

The results obtained using 4% metaldehyde as the molluscicide are summarized in Table 1. The mean data represent the results of three terraria trials and demonstrate % slug mortality and % grain loss obtained using different bird repellent additives. A certain amount of grain loss is recorded representing ungerminated or non-viable grains. The relative performance of bird repellents against each other and the control pellets is shown in Figures 1 to 3.

As can be seen the anthranilate and d-pulegone compounds enhance the molluscicidal efficacy at the concentrations added compared to the metaldehyde alone pellets. Methyl anthranilate is more efficacious at a concentration of 0.5% than at 1% and most of the repellents were more efficient at the lower concentration of 0.5%. The best performance was recorded for d-pulegone which achieved a 100% mortality rate at a concentration of 0.5% in 4% metaldehyde by the third day of exposure. D-Pulegone performed slightly better than methyl anthranilate (MA) when used at the 1% level. The repellents dimethyl anthranilate (DMA) and a starch encapsulated mixture of MA/DMA were found to closely follow D-pulegone and MA in terms of improved molluscicidal efficacy.

A comparison of the efficacy obtained at 2% metaldehyde and 4% metaldehyde using a 1% concentration of bird repellent additive was carried out using a similar experimental technique as before. Figure 4 shows that overall 4% metaldehyde formulations are the most efficacious with d-pulegone and methyl anthranilate showing the greatest synergistic effect. Formulations containing 6% metaldehyde by weight are also envisaged.

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Other animal repellent compounds such as Bitrex and Cinnamamide were not found to enhance the molluscicidal efficacy over that of the 4% metaldehyde alone formulation at the concentrations used.

CLAIMS:

1. A molluscicide formulation containing a non-toxic animal repellent and metaldehyde.
2. A formulation as claimed in claim 1, in which the animal repellent is a bird and/or mammal repellent.
3. A formulation as claimed in claim 1 or claim 2, in which the repellent is an anthranilate compound.
4. A formulation as claimed in claim 3, in which the repellent is selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate and dimethyl anthranilate.
5. A formulation as claimed in claim 2, in which the repellent is methyl anthranilate.
6. A formulation as claimed in claim 2, in which the repellent is dimethyl anthranilate.
7. A formulation as claimed in claim 1 or claim 2, in which the repellent is d-pulegone.
8. A formulation as claimed in any preceding claim, in which the repellent is present at a concentration of not more than 1%.
9. A formulation as claimed in any preceding claim, in which the repellent is present at a concentration of not more than 0.5%.
10. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 6%.

11. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 4%.

12. A formulation as claimed in any preceding claim, in which the metaldehyde is present at a concentration of not more than 2%.

13. A method of use of a molluscicide formulation comprising a non-toxic animal repellent and metaldehyde.

14. A method as claimed in claim 13, in which the animal repellent is selected from: methyl anthranilate, isobutyl anthranilate, ethyl anthranilate, isobutyl methyl anthranilate, dimethyl anthranilate and d-pulegone.

15. A method as claimed in claim 14, in which the repellent is present at a concentration of not more than 1 %.

16. A method as claimed in claim 14, in which the repellent is present at a concentration of not more than 0.5%.

17. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 6%.

18. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 4%.

19. A method as claimed in any of claims 13-16, in which the metaldehyde is present at a concentration of not more than 2%.

20. A molluscicide formulation consisting of 92-96.5% flour, 6-2% metaldehyde, 1-0.5% non-toxic repellent and 1% calcium propionate.

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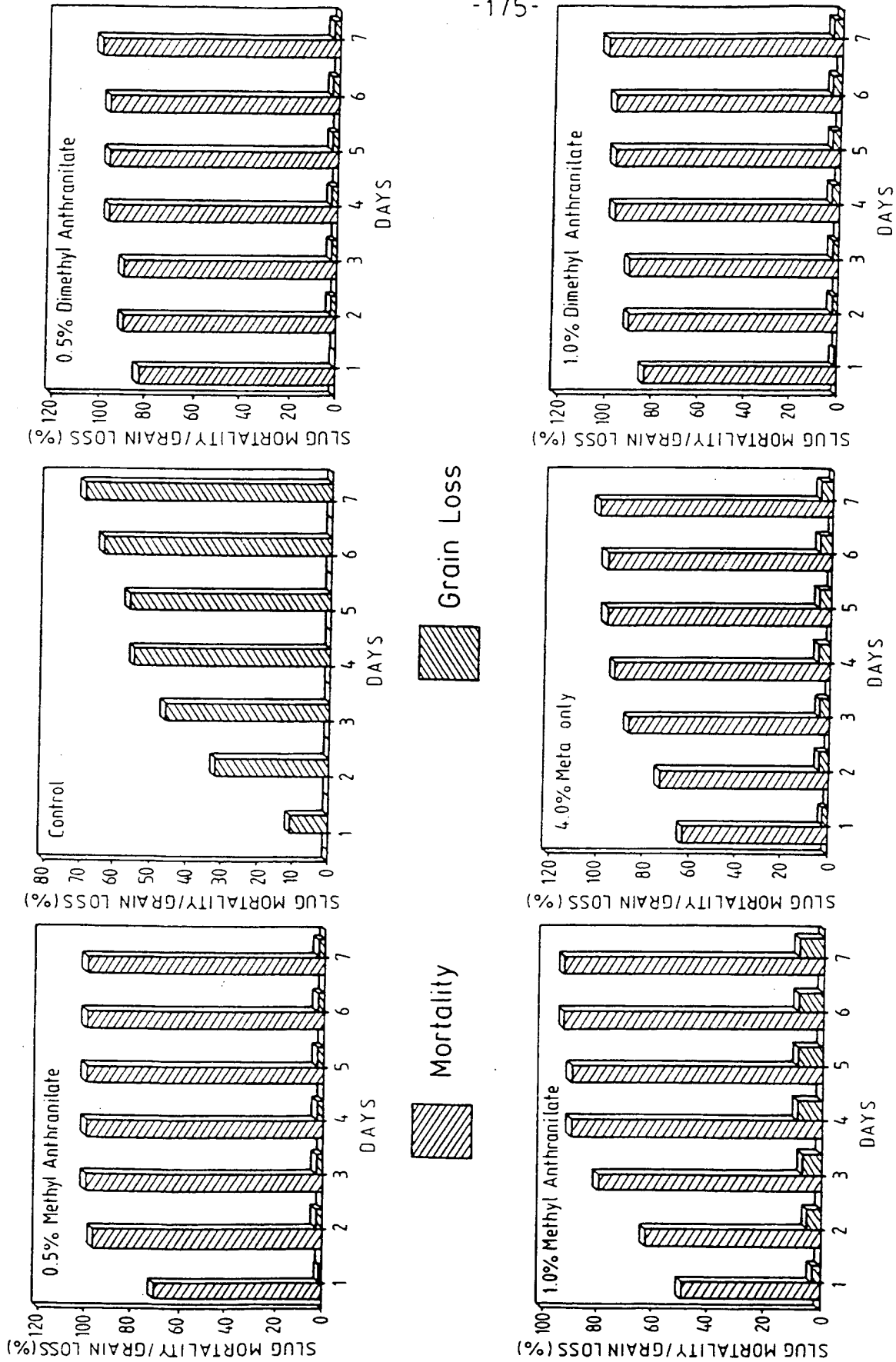


FIG. 1

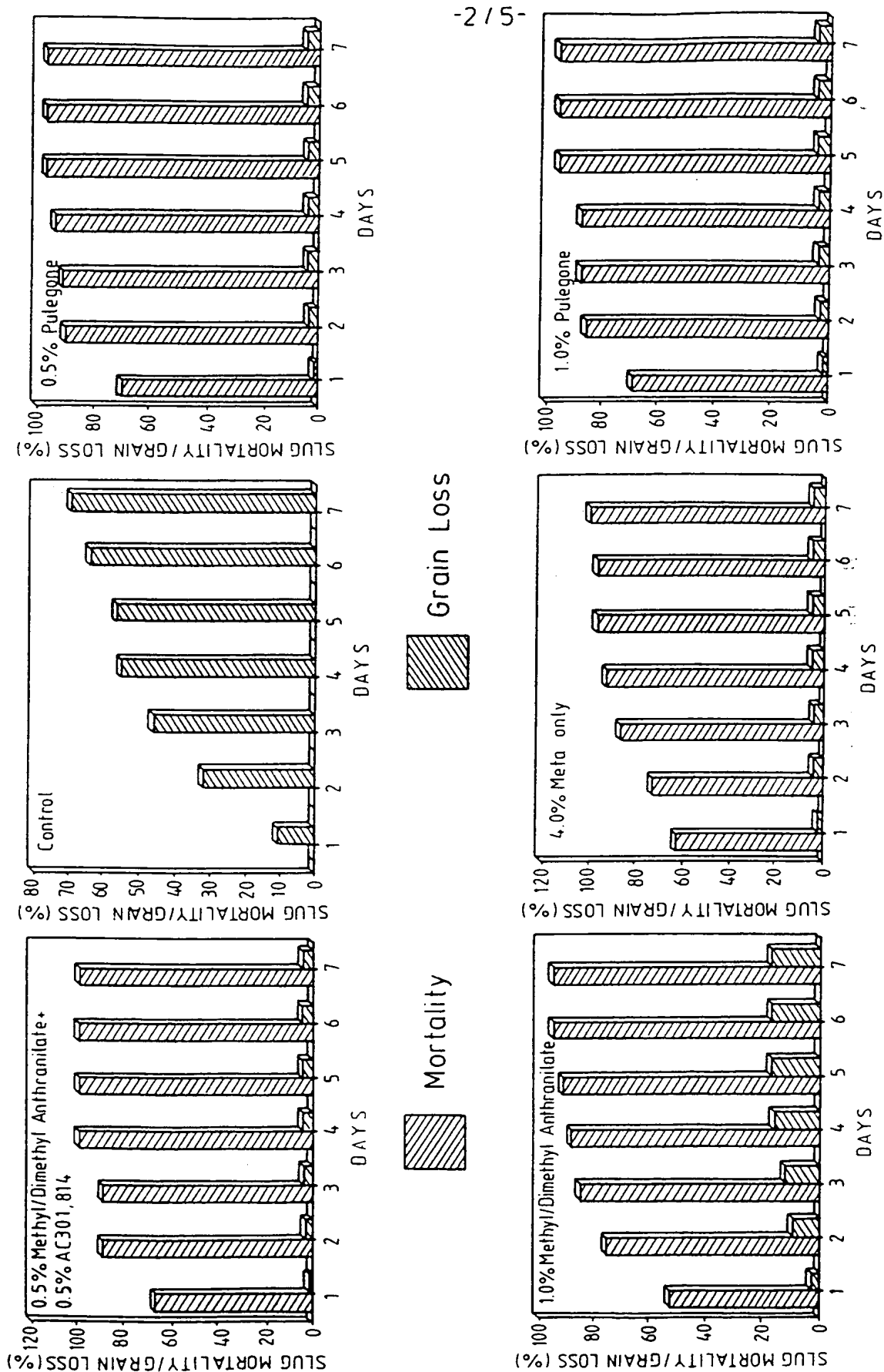


FIG. 2

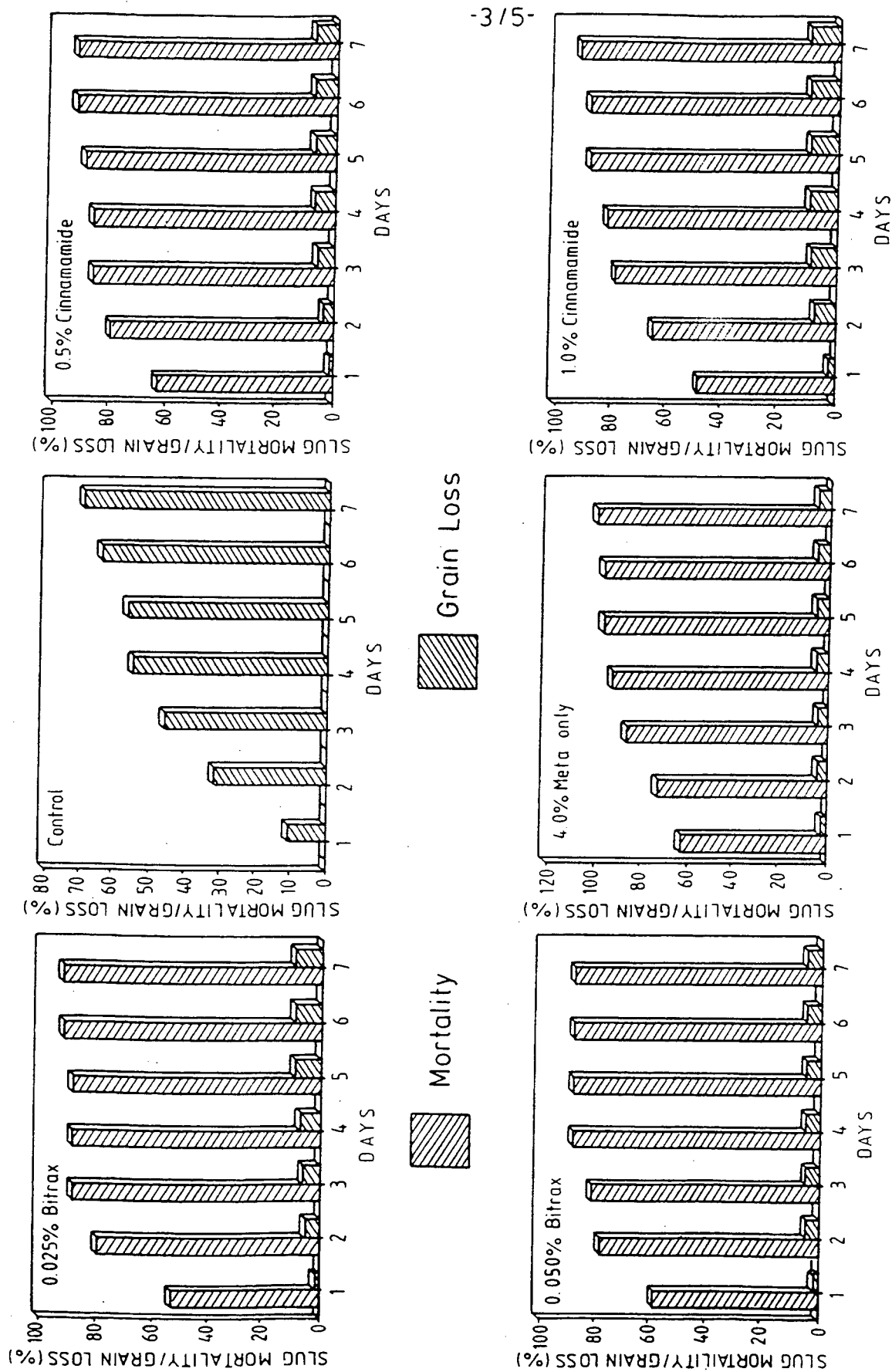


FIG. 3

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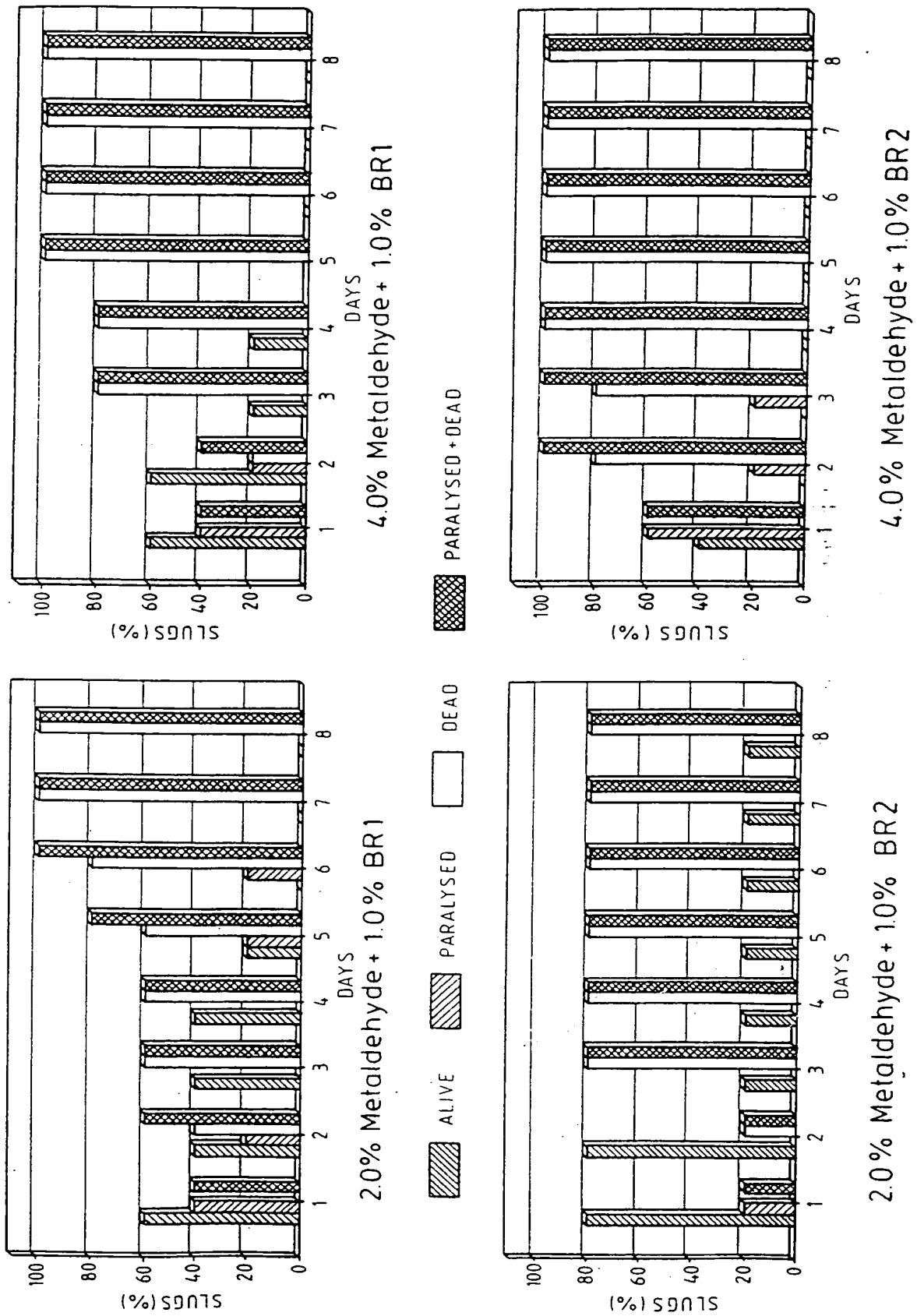


FIG. 4

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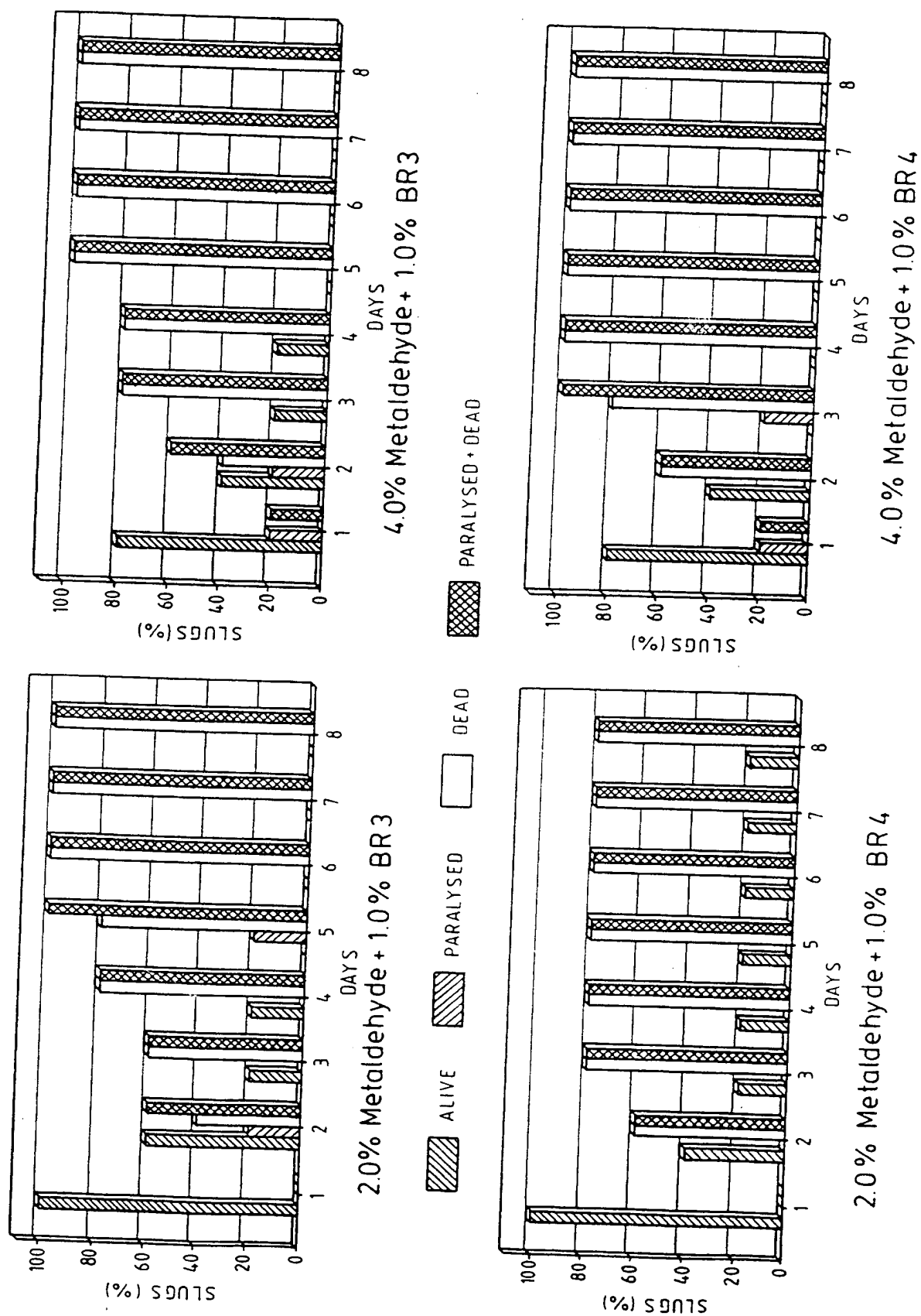


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01258

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N35/02 A01N25/00 //(A01N35/02, 37:44, 35:06)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 314 846 A (R & C PRODUCTS PTY LTD) 10 May 1989	1,2, 8-13, 17-19
Y	see page 2, line 11 - line 51 see page 4, line 13 - line 44; claims 1-5,10 --- -/--	3-7, 14-16,20



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Int ional Application No

PCT/GB 98/01258

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 122, no. 17, 24 April 1995 Columbus, Ohio, US; abstract no. 207728, MASTROTA, F. NICHOLAS ET AL: "Evaluation of taste repellents with northern bobwhites for deterring ingestion of granular pesticides." XP002077132 see abstract & ENVIRON. TOXICOL. CHEM. (1995), 14(4), 631-8 CODEN: ETOCDK; ISSN: 0730-7268, 1995, ----	3-5, 7, 14-16
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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